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claims and to be republished in the event of the receipt of
amendments.*(54) Title: PROCESS USING CF₂I₂ AND OLEFINS FOR PRODUCING DIIDO FLUOROCOMPOUNDS, AND PRODUCTS
THEREOF

(57) Abstract

A process is disclosed for making diiodofluorinated compounds of the formula ICF₂(A)_nI wherein n is an integer of at least 1 and each A is CX₁YCQZ wherein each X, Y, Q and Z are each independently selected from the group consisting of H, F, Cl, R_F and OR_F, and R_F is a perfluoroalkyl group or perfluorinated polyether group wherein one or more of the fluorines is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride. The process involves reacting an olefin of the formula CXY = CQZ with CF₂I₂ at a temperature in the range of from about 120 °C to 240 °C. Diiodofluorinated compounds of the formula ICF₂CH₂CHR_FI are also disclosed.

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TITLEPROCESS USING CF_2I_2 AND OLEFINS FOR PRODUCING DIIDO
FLUOROCOMPOUNDS, AND PRODUCTS THEREOFFIELD OF THE INVENTION

5 This invention relates to diiodofluorinated compounds and their production, and more particularly to using CF_2I_2 and olefinic compounds as reactants for producing diiodofluorinated compounds.

BACKGROUND

10 Diiodoperfluoroalkanes are useful as chain transfer reagents for fluoroelastomers and in the free radical polymerization of fluorinated vinyl monomers. See U.S. Patent Nos. 4,243,770 and 4,361,678. The reaction of CF_2I_2 with olefins allows the stepwise addition to the chain, thereby providing controlled chain growth. The production of these diiodoperfluoroalkanes at relatively high yields has been hampered in the past by the lack of a method by
15 which to produce relatively high yield and purity CF_2I_2 . However, as described in commonly held U.S. Patent Application No. 60/012,160, filed February 23, 1996, CF_2I_2 can be produced in sufficiently high yields to facilitate the reactions described below.

Commonly held U.S. Patent No. 5,504,248 describes the production of
20 diiodofluoroalkanes by reacting I_2 with hexafluorocyclopropane. This process involves a relatively complex ring-opening reaction, and uses relatively expensive starting materials.

Elsheimer, et al., J. Org. Chem. 1984, 49, pp. 205-207, discloses reactions of CF_2I_2 with hydrocarbon olefins to produce iododifluoroalkenes via photolysis,
25 or diiododifluoroalkanes via reactions catalyzed by peroxide at temperatures less than 100°C . The use of peroxides to form the diiododifluoroalkanes could result in the production of other reaction products, which would have to be separated from the desired products, thus adding an additional step, as well as the associated costs involved with such purification.

30 Many citations are found throughout the literature describing diiodofluorinated compounds, but interest continues in developing new, efficient processes for producing selected diiodofluorinated compounds.

SUMMARY OF THE INVENTION

A process is provided for making diiodofluorinated compounds of the
35 formula $\text{ICF}_2(\text{A})_n\text{I}$ wherein n is an integer of at least 1 and each A is $\text{CX}_1\text{Y}_1\text{CQ}_1\text{Z}_1$ wherein each X_1 , Y_1 , Q_1 , and Z_1 are each independently selected from the group consisting of H, F, Cl, R_F and OR_F , and R_F is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to

20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride. The process comprises
5 reacting an olefin of the formula $CXY=CQZ$ with CF_2I_2 at a temperature in the range of from about 120°C to 240°C.

Diiodofluorinated compounds of the formula $ICF_2CH_2CHR_FI$, where R_F is as indicated above, are also provided in accordance with this invention.

DETAILED DESCRIPTION

10 This invention provides a process by which CF_2I_2 is reacted with olefins to produce diiodofluorinated compounds, generally described in Equation (I) below:



15 In Equation (I), A represents $(CXYCQZ)$, and X, Y, Q and Z are each independently H, F, Cl, R_F or OR_F , and preferably at least one of X, Y, Q and Z is F. The number of repeat units of A, as represented by n in Equation (I) is 1 or greater and is preferably from 1 to about 5, more preferably from 1 to 3. Of note
20 are embodiments where n is 1; embodiments where n is 2; and embodiments where n is 3.

The process represented by Equation (I) takes place at an elevated temperature. It has been found in accordance with this invention that when
25 conducted at temperatures of about 120°C or above, the reaction needs no chemical catalyst or initiator to proceed. Indeed, the process of this invention is typically conducted in the substantial absence of a catalyst or initiator. By "substantial absence of catalyst or initiator" is meant that the reaction would effectively proceed even in the absence of any catalyst or initiator which might be added. By "catalyst or initiator" is meant materials or chemicals such as, for
30 example, peroxides or azo compounds, which have been previously required to produce diiodofluorinated compounds at lower temperatures.

The temperature range is generally between about 120°C and about 240°C, and is preferably between about 170°C and about 190°C. The process can take
35 place in the liquid or gas phase. Liquid phase reactions may be conducted in solution in inert solvents such as, for example, fluorocarbons, fluorochlorocarbons and hydrofluorocarbons, or (preferably) may be conducted neat. Although not necessary, if the reaction is carried out in the liquid state, moderate agitation is preferred. It is also preferred that oxygen and water are excluded from the

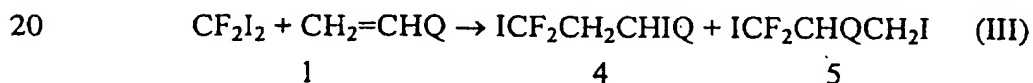
reaction, and it may be convenient to carry out the reaction under an inert gas blanket, such as nitrogen.

Pressure is not critical, autogenous pressure (of all the ingredients) being generally the convenient operation pressure. Typically, the reaction is conducted
 5 at pressure within the range of from about 20 psi (about 138 Pa) to about 1000 psi (about 6900 Pa). Non-limiting examples of reaction vessels include shaker tubes, tanks, autoclaves and reactors.

It is noted that for each addition of olefinic starting material, the unit A can have either of two orientations, with either carbon involved with the olefinic bond,
 10 attaching to the end carbon of the iodo reactant. Accordingly, where the carbons involved with the olefinic bond are differently substituted, the addition of each A group can result in either of two products. Thus for example, when n is 1, the reaction can be represented as:

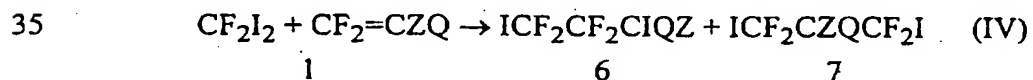


When X, Y and Z are each H in Equation (II), the reaction may be represented by Equation (III) below:



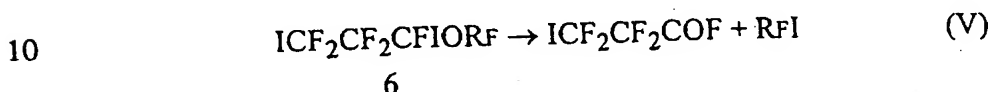
Both fluorinated or non-fluorinated olefins, as determined by the composition of Q, give relatively good yields of adducts. When reacted with ethylene, a
 25 relatively higher yield of adduct 4 is obtained, as described in Example 1 below. A mixture of regioisomers 4 and 5 is, however, formed with propylene and vinyl fluoride (Examples 2 and 8, respectively). Fluoroalkyl substituted olefins or fluorinated polyether substituted olefin such as $\text{CH}_2=\text{CHR}_F$ where R_F is highly fluorinated (Examples 3 and 4) also undergo an addition reaction with CF_2I_2 to
 30 give 4 exclusively. Examples of highly fluorinated R_F groups include $\text{CF}_2\text{CF}_2\text{Br}$, $\text{CF}_2\text{CF}_2\text{I}$, and perfluoroalkyl groups (e.g., C_4F_9 , C_6F_{13} and C_8F_{17} groups).

Preferably at least one of X, Y, Z and Q is F. When X and Y are each F in Equation (I), the reaction may be represented by Equation (IV) below:

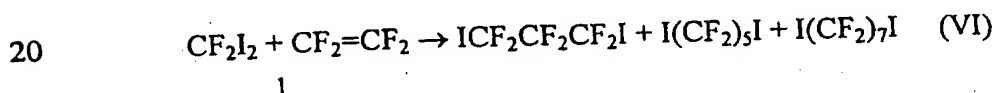


Of note are embodiments of Equation (IV) where Q is F, H, R_F or OR_F and embodiments where Z is F. Fluorinated olefins such as $\text{CF}_2=\text{CFH}$, $\text{CF}_2=\text{CFCF}_3$
 40 and $\text{CF}_2=\text{CH}_2$ give mixtures of regioisomers 6 and 7. Unlike other perfluoroalkyl iodides, CF_2I_2 cleanly adds to perfluorovinyl ethers of the formula $\text{CF}_2=\text{CFOR}_F$

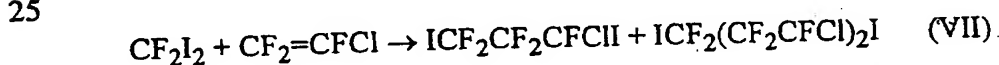
to give compound 6 ($Q = OR_F$), along with small amounts of compound 7 ($Q = OR_F$). The functional groups such as ester, sulfonyl fluoride and nitrile in the vinyl ethers do not interfere with the addition reaction, so that various functional diiodocompounds may be prepared, as found in Examples 12-15. When the reaction mixture of fluorovinyl ethers and CF_2I_2 is subjected to prolonged heating, as in Examples 12 and 15, the initially formed compound 6, in Equation (V) below, where $Q = OR_F$, decomposes to ICF_2CF_2COF and R_FI (see also U.S. Patent No. 5,504,248).



The addition of R_FI to tetrafluoroethylene (TFE), as shown in Example 5, gives a broad distribution of telomers. See also Chemistry of Organic Fluorine Compounds, 2nd Ed. M. Hudlicky, 1992, p. 420-427). While CF_2I_2 reacts with TFE, the main product is a 1:1 adduct ($ICF_2CF_2CF_2I$) with only small amounts of 1:2 adduct ($I(CF_2)_5I$) and trace of 1:3 adduct ($I(CF_2)_7I$), as shown in Equation (VI) below:



When $CF_2=CFCl$ is reacted with CF_2I_2 , a mixture of 1:1 and 1:2 adducts is formed, as shown in Equation (VII) below, where $n=2$.



Other higher homologs are also formed (e.g., n is 3, 4, etc.). In general, higher ratios of olefinic starting materials to CF_2I_2 yield higher telomers (i.e., n is higher). The degree of telomerization is limited by product solidification. Preferably, the ratio of olefinic starting material to CF_2I_2 is from about 1:1 to 5:1.

The diiodocompounds formed by the instant process, when one of X, Y, Z or Q is a functional group as represented by RF or OR_F , may be used to chain extend or graft the resulting polymer onto another polymer, or to react to form a specific chain end which may act to change the polymer's surface properties. One example of this would be the production of a potential surfactant material when RF is a fluorinated ester or fluorinated sulfonyl group.

Compounds provided by this invention include compounds where each A is (CH_2CHR_F) . Of note are compounds of this type having the formula

$$40 \quad ICF_2CH_2CHR_FI.$$

In the Examples below, unless otherwise specified, all reagents were used as received from Aldrich Chemical Co., Milwaukee, WI. CF_2I_2 was made according to the procedure as described in co-pending U.S. Patent Application No. 60/012,160.

- 5 Gas chromatography (GC) was performed on an HP 5890 II Plus gas chromatograph (Hewlett Packard, Wilmington, DE), using a 20% OV-210 column (Supelco, Bellefonte, PA), with an initial temperature of 50°C, a final temperature of 250°C, and a rate of 15°C/min. The ^1H and ^{19}F nuclear magnetic resonance (NMR) data were obtained using a GE Plus NMR spectrometer (General Electric, Schenectady, NY). All measurements are relative to deuterated chloroform (CDCl_3). Ratios given are those for peak areas by GC or molar ratios based on NMR data as designated in the specific examples. High resolution mass spectrometry (HRMS) was done using a Micromass-7070H (VG Analytical, Manchester, UK).
- 10 The reaction products were obtained by distillation, and their boiling points (bp, °C) were obtained. Elemental analyses were obtained by routine methods.

The following abbreviations are used in the Examples below:

- s = singlet NMR peak
20 d = doublet NMR peak
t = triplet NMR peak
m = multiplet NMR peak

EXAMPLE 1

Reaction of CF_2I_2 with ethylene

- 25 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C. The tube was evacuated and then 4.0 g of ethylene was added. After the tube was heated at 185°C for 5 hour, 30.3 g of crude product was obtained which was distilled to give 27.3 g of adduct with 100% GC purity, bp 94-95°C/ 50 mmHg. ^{19}F NMR: -39.1 (t, $J = 14.3$ Hz); ^1H NMR: 3.21 (t, $J = 7.3$ Hz, 2H), 30 2.95 (m, 2H). HRMS: calcd for $\text{C}_3\text{H}_4\text{F}_2\text{I}_2$: 331.8371. Found: 331.8336. Anal: calcd for $\text{C}_3\text{H}_4\text{F}_2\text{I}_2$: C, 10.86; H, 1.21; F, 11.45; I, 76, 48. Found: C, 10.84; H, 1.25; F, 11.59; I, 75.96.

EXAMPLE 2

Reaction of CF_2I_2 with propylene

- 35 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to -78°C. The tube was evacuated and then 5.0 g of propylene was added. After the tube was heated at 185°C for 5 hour, 31.6 g of crude product was obtained which was distilled to give 28.7 g of product, bp 106-107°C/ 4.8 mmHg. GC and NMR

- indicated a mixture of $\text{ICF}_2\text{CH}_2\text{CHICH}_3$ and $\text{ICH}_2\text{CH}(\text{CF}_2\text{I})\text{CF}_3$ in a ratio of 13 to 1. ^{19}F NMR: for major product: -35.4 (ddd, $J = 173$ Hz, $J = 18.4$ Hz, $J = 8.7$ Hz, 1F), -38.3 (dt, $J = 173$ Hz, $J = 16.4$ Hz, 1F). ^1H NMR: 4.35 (m, 1H), 3.28 (m, 1H), 2.90 (m, 1H), 2.00 (d, $J = 7.0$ Hz, 3H). HRMS: calcd for $\text{C}_4\text{H}_7\text{F}_2\text{I}_2$: 345.8527. Found: 345.8565 for $\text{ICF}_2\text{CH}_2\text{CHICH}_3$ and 345.8510 for $\text{ICH}_2\text{CH}(\text{CF}_2\text{I})\text{CH}_3$. Anal: calcd for $\text{C}_4\text{H}_7\text{F}_2\text{I}_2$: C, 13.89; H, 1.75; F, 10.98; I, 73.38. Found: C, 13.99; H, 1.98; F, 10.80; I, 73.34.

EXAMPLE 3

Reaction of CF_2I_2 with 4-bromo-3,3,4,4-tetrafluorobutene-1

- 10 A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and 21.0 g of $\text{BrCF}_2\text{CF}_2\text{CH}=\text{CH}_2$ and cooled to -78°C . The tube was evacuated and then heated at 180°C for 2.5 hour. 31.6 g of crude product was obtained which was washed with aqueous Na_2SO_3 solution and distilled to give 28.7 g of $\text{ICF}_2\text{CH}_2\text{CHICF}_2\text{CF}_2\text{Br}$, bp $53^\circ\text{C}/19$ mmHg. ^{19}F NMR: -36.7 (ddd, $J = 176.1$ Hz, $J = 16.2$ Hz, $J = 7.1$ Hz, 1F), -39.7 (dt, $J = 176$ Hz, $J = 15.8$ Hz, 1F), -59.9 (dd, $J = 178.6$ Hz, $J = 7.6$ Hz, 1F), -61.0 (dd, $J = 178.6$ Hz, $J = 5.6$ Hz, 1F), -94.6 (dt, $J = 260.6$ Hz, $J = 7.2$ Hz, 1F), -109.8 (ddd, $J = 261.0$ Hz, $J = 18$ Hz, $J = 7.4$ Hz, 1F).

EXAMPLE 4

Reaction of CF_2I_2 with 4-iodo-3,3,4,4-tetrafluorobutene-1

- 20 A 75 mL of shaker tube was charged with 42.3 g of 1:1 mixture of CF_2I_2 and $\text{ICF}_2\text{CH}_2\text{CH}=\text{CH}_2$ and cooled to -78°C . The tube was evacuated and then heated at 180°C for 2.5 hour. 36 g of crude product was obtained, which was washed with aqueous Na_2SO_3 solution and distilled to give 23.5 g of $\text{ICF}_2\text{CH}_2\text{CHICF}_2\text{CF}_2\text{I}$, bp $118-120^\circ\text{C}/10$ mmHg. ^{19}F NMR: -36.7 (ddd, $J = 175.5$ Hz, $J = 16.0$ Hz, $J = 7.7$ Hz, 1F), -39.6 (dt, $J = 175.5$ Hz, $J = 16.0$ Hz, 1F), -54.8 (ddt, $J = 202.2$ Hz, $J = 7.3$ Hz, $J = 2.3$ Hz, 1F), -56.0 (dd, $J = 203.0$ Hz, $J = 7.0$ Hz, 1F), -88.3 (dt, $J = 261.0$ Hz, $J = 7.0$ Hz, 1F), -106.2 (ddd, $J = 261.0$ Hz, $J = 19$ Hz, $J = 8.4$ Hz, 1F).

EXAMPLE 5

Reaction of CF_2I_2 with tetrafluoroethylene

- 30 A 400 mL of shaker tube was charged with 152 g of CF_2I_2 and cooled to -78°C . After the tube was evacuated and then heated to 185°C , 20 g of TFE was added and the tube kept at 185°C for 2 hours. Additional 20 g of TFE was added and the tube was kept for 2 hours. Finally, 10 g of TFE was added and the tube kept for 6 hours. 192.3 g of crude products were obtained and GC indicated that a mixture of 82% $\text{I}(\text{CF}_2)_3\text{I}$ and 7% $\text{I}(\text{CF}_2)_5\text{I}$. Distillation gave 169.6 g of $\text{I}(\text{CF}_2)_3\text{I}$ with 2.5% of $\text{I}(\text{CF}_2)_5\text{I}$, bp $76-80^\circ\text{C}/150$ mmHg, and 13.1 g of high boiling residue containing 20% $\text{I}(\text{CF}_2)_3\text{I}$, 70% $\text{I}(\text{CF}_2)_5\text{I}$ and 5% $\text{I}(\text{CF}_2)_7\text{I}$. ^{19}F NMR for $\text{I}(\text{CF}_2)_3\text{I}$:

-58.2 (t, J = 4.7 Hz, 4F), -105.2 (t, J = 4.7 Hz, 2F); for I(CF₂)₅I: -59.4 (t, J = 4.6 Hz, 4F), -113.6 (s, 4F), -120.6 (m, 2F).

EXAMPLE 6

Reaction of CF₂I₂ with trifluoroethylene

- 5 A 75 mL of shaker tube was charged with 30.5 g of CF₂I₂ and cooled to -78°C. The tube was evacuated and then 16.0 g of trifluoroethylene was added. After the tube was heated at 185°C for 10 hour, GC indicated 70% of conversion and 26.3 g of crude product was obtained which was washed with aqueous Na₂SO₃ solution and distilled to give 1.5 g of 55% pure of adduct, 2.5 g of 84%
 10 pure adduct and 12.8 g of pure product bp 83°C/80 mmHg. ¹⁹F NMR and GC indicated a mixture ICF₂CHFCF₂I and ICF₂CF₂CHFI in a ratio of 1.5 to 1. ¹⁹F NMR: ICF₂CHFCF₂I: -52.6 (dm, J = 207.8 Hz, 2F), -54.8 (dm, J = 207.8 Hz, 2F), -176.2 (m, 1F); ICF₂CF₂CHFI: -57.9 (dm, J = 207.8 Hz, 1F), -59.8 (dt, J = 207.8 Hz, J = 6.5 Hz, 1F), -101.0 (ddt, J = 273.1 Hz, J = 32.3 Hz, J = 6.3 Hz, 1F),
 15 -116.3 (dm, J = 273.1 Hz, 1F), -165.7 (m, 1F). HRMS: calcd. for C₃HF₅I₂: 385.8088. Found: 385.8023. Anal: calcd for C₃HF₅I₂: C, 9.34; H, 0.26; F, 24.62; I, 65.78. Found: C, 9.25; H, 0.27; F, 24.39; I, 65, 81.

EXAMPLE 7

Reaction of CF₂I₂ with vinylidene fluoride

- 20 A 75 mL of shaker tube was charged with 30.5 g of CF₂I₂ and cooled to -78°C. The tube was evacuated and then 10.0 g of CF₂=CH₂ was added. After the tube was heated at 185°C for 8 hour, GC indicated 10% CF₂I₂ and 79.5% of adduct (area ratio). 35.1 g of crude products were obtained which was distilled to give 4.1 g of 50% pure of adduct and 26.4 g of pure adduct, bp
 25 80-81°C/60 mmHg. ¹⁹F NMR and GC indicated a mixture ICF₂CH₂CCF₂I and ICF₂CF₂CH₂I in a ratio of 27.6 to 1. ¹⁹F NMR: ICF₂CH₂CF₂I: -39.6 (m); ICF₂CF₂CH₂I: -59.6 (t, J = 4 Hz, 2F), -101.5 (t, J = 16.4Hz, 2F). HRMS: Calcd for C₃H₂F₄I₂: 367.8182. Found: 367.8168 for ICF₂CH₂CF₂I; 367.8150 for ICF₂CF₂CH₂I. Anal: calcd for C₃H₂F₄I₂: C, 9.80; H, 0.55; I, 69.00. Found: C,
 30 9.76; H, 0.62; I, 68.48.

EXAMPLE 8

Reaction of CF₂I₂ with vinyl fluoride

- A 75 mL of shaker tube was charged with 30.5 g of CF₂I₂ and cooled to -78°C. The tube was evacuated and then 6.0 g of vinyl fluoride was added. After
 35 the tube was heated at 185°C for 5 hour, GC indicated 90% of conversion and 27.8 g of crude product was obtained which was distilled to give 4.9 g of 55% pure of adduct and 17.1 g of pure product, bp 87-89°C/50 mmHg. ¹⁹F NMR and GC indicated a mixture ICF₂CH₂CCFHI and ICF₂CFHCH₂I in a ratio of 8.6 to 1.

- ^{19}F NMR: $\text{ICF}_2\text{CH}_2\text{CHFI}$: -37.6 (dm, $J = 178.5$ Hz, 1F), -40.33 (dm, $J = 178.5$ Hz, 1F), -144.7 (m, 1F); $\text{ICF}_2\text{CFHCH}_2\text{I}$: -51.8 (ddd, $J = 195.5$ Hz, $J = 21.0$ Hz, $J = 7.4$ Hz, 1F), -56.3 (ddd, $J = 196$ Hz, $J = 21.7$ Hz, $J = 7.3$ Hz, 1F), -176.8 (m, 1F).
 HRMS: calcd for $\text{C}_3\text{H}_3\text{F}_3\text{I}_2$: 349.8280. Found: 349.8391 for $\text{ICF}_2\text{CH}_2\text{CHFI}$;
 5 349.8307 for $\text{ICF}_2\text{CFHCH}_2\text{I}$. Anal: calcd for $\text{C}_3\text{H}_3\text{F}_3\text{I}_2$: C, 10.30; H, 0.86.
 Found: C, 10.26; H, 1.00.

EXAMPLE 9

Reaction of CF_2I_2 with hexafluoropropylene

- A 75 mL of shaker tube was charged with 45.6 g of CF_2I_2 and cooled to
 10 -78°C . The tube was evacuated and then 24.0 g of hexafluoropropylene was
 added. After the tube was heated at 185°C for 12 hour, GC indicated 55% of
 conversion and 40.1 g of crude were washed with aqueous Na_2SO_3 solution and
 then distilled to give 6.2 g of 82% pure of CF_2I_2 , 2.7 g of a mixture of 60% of
 CF_2I_2 and 28% of $\text{ICF}_2\text{CF}_2\text{CFICF}_3$, bp $40-63^\circ\text{C}/95$ mmHg, 3.0 g of a mixture of
 15 23% of CF_2I_2 and 62% of $\text{ICF}_2\text{CF}_2\text{CFICF}_3$, bp $64-71^\circ\text{C}/95$ mmHg and 10.6 g of
 93% pure $\text{ICF}_2\text{CF}_2\text{CFICF}_3$, bp $74-76^\circ\text{C}/95$ mmHg. HRMS: calcd for $\text{C}_4\text{F}_8\text{I}_2$:
 453.7962. Found: 453.7915 for $\text{ICF}_2\text{CF}_2\text{CFICF}_3$; 3452.7967 for $(\text{ICF}_2)_2\text{CFCF}_3$.

EXAMPLE 10

Reaction of CF_2I_2 with perfluoromethyl vinyl ether

- A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to
 20 -78°C . The tube was evacuated and then 22.0 g of perfluoromethyl vinyl ether
 was added. After the tube was heated at 185°C for 3.5 hour, GC indicated 76% of
 conversion and 37.2 g of crude products were distilled to give 13.8 g of 47.6% of
 CF_2I_2 and 46.7% of adduct, bp $50-79^\circ\text{C}/100$ mmHg and 18.4 g of 99% pure
 25 adduct, bp $87-89^\circ\text{C}/50$ mmHg. ^{19}F NMR and GC indicated a mixture
 $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$ and $(\text{ICF}_2)_2\text{CFOCF}_3$ in a ratio of 12 to 1. ^{19}F NMR for
 $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$: -55.0 (dm, $J = 204.1$ Hz, 1F), -55.3 (d, $J = 11.3$ Hz, 3F),
 -58.4 (ddm, $J = 205$ Hz, $J = 26.4$ Hz, 1F), -68.0 (m, 1F), -102.6 (dt, $J = 276.2$ Hz, J
 = 7.7 Hz, 1F), -104.2 (dt, $J = 276.4$ Hz, $J = 7.2$ Hz, 1F); for $(\text{ICF}_2)_2\text{OCF}_3$: -51.7
 30 (m, 3F), -53.9 (m, 4F), -124.2 (m, 1F); HRMS: calcd for $\text{C}_4\text{F}_8\text{I}_2\text{O}$: 469.7911.
 Found: 469.7930 for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_3$; 469.7967 for $(\text{ICF}_2)_2\text{CFOCF}_3$.

EXAMPLE 11

Reaction of CF_2I_2 with perfluoropropyl vinyl ether

- A 75 mL of shaker tube was charged with 30.5 g of CF_2I_2 and cooled to
 35 -78°C . The tube was evacuated and then 60.0 g of perfluoropropyl vinyl ether
 was added. After the tube was heated at 185°C for 3.5 hour, 78.5 g of crude
 products were distilled to give 29.0 g of perfluoropropyl vinyl ether; 6.2 g of 72%
 pure of adduct, bp $30-80^\circ\text{C}/40$ mmHg; 27.6 g of pure adduct, bp

- 83-84°C/40 mmHg; and 4.4 g of 68% pure adduct, bp 85°C/40 mmHg to 74°C/15 mmHg. Yield 79%. ¹⁹F NMR and GC indicated a mixture ICF₂CF₂CFIOCF₂CF₂CF₃ and (ICF₂)₂CFOCF₂CF₂CF₃ in a ratio of 85.4 to 13.6. ¹⁹F NMR for ICF₂CF₂CFIOCF₂CF₂CF₃: -55.3 (d, J = 204.6 Hz, 1F), -58.8 (ddd, J = 204.6 Hz, J = 27 Hz, J = 6.3 Hz, 1F), -68.7 (m, 1F), -81.3 to -81.9 (m, 4F), -90.7 (d, J = 147.6 Hz, 1F), -102.4 (dt, J = 276.7 Hz, J = 8 Hz, 1F), -104.4 (dt, J = 276.6 Hz, J = 7.5 Hz, 1F), -130.4 (s, 2F). (ICF₂)₂OCF₂CF₂CF₃: -53.8 (m, 4F), -79.4 (m, 2F), -81.3 (M, 3F), -122.3 (m, 1F), -129.3 (M, 2F). HRMS: calcd for C₆F₁₂I₂O: 569.7847. Found: 442.8824 for ICF₂CF₂CFIOCF₂CF₂CF₃-I; 569.7796 for (ICF₂)₂CFOCF₂CF₂CF₃. Anal: calcd for C₆F₁₂I₂O: C, 12.65; I, 44.55. Found: C, 12.72; I, 44.23.

EXAMPLE 12

Reaction of CF₂I₂ with CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CO₂Me

- A 240 mL of shaker tube was charged with 30.5 g of CF₂I₂ and 60.0 g of CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CO₂Me and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 3.5 hour. 82.2 g of a mixture of 5% of ICF₂CF₂COF, 4% of CF₂I₂, 31% of CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CO₂Me, 9% ICF₂CF(CF₃)OCF₂CF₂CO₂Me and 51% adduct were obtained (GC area). Distillation gave 12.3 g of mainly CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CO₂Me, bp 40-88°C/60 mmHg, 8.6 g of material containing 45% CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CO₂Me and 55% of ICF₂CF(CF₃)OCF₂CF₂CO₂Me, bp 82°C/50 mmHg to 102°C/4 mmHg, and 45.9 g of adduct, bp 103-110°C/3 mmHg. The adduct was a mixture of ICF₂CF₂CFIOCF₂CF(CF₃)OCF₂CF₂CO₂Me and (ICF₂)₂CFOCF₂CF(CF₃)OCF₂CF₂CO₂Me.

EXAMPLE 13

Reaction of CF₂I₂ with CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CN

- A 240 mL of shaker tube was charged with 30.5 g of CF₂I₂ and 45.0 g of CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CN and cooled to -78°C. After being evacuated at -78°C, the tube was heated at 185°C for 4 hour. 67.8 g of crude products were obtained. Distillation gave 15 g of mainly CF₂=CFOCF₂CF(CF₃)OCF₂CF₂CN, bp 85-100°C, 37.6 g of adduct, bp 115-116°C/30 mmHg. The adduct was a mixture of ICF₂CF₂CFIOCF₂CF(CF₃)OCF₂CF₂CN and (ICF₂)₂CFOCF₂CF(CF₃)OCF₂CF₂CN in a ratio of 5.7 to 1. ¹⁹F NMR for ICF₂CF₂CFIOCF₂CF(CF₃)OCF₂CF₂CN: -55.5 (d, J = 205.2 Hz, 1F), -58.9 (ddd, J = 205.5 Hz, J = 27.3 Hz, J = 6.0 Hz, 1F), -69.4 (m, 1F), -79.1 to -80.4 (m, 4F), -84.1 to -85.2 (m, 2F), -90.0 (dm, J = 152.5 Hz, 1F), -102.0 (dm, J = 277.7 Hz, 1F), -104.5 (dm, J = 277.7 Hz, 1F), -108.6 (m, 2F), -145.1 (t, J = 21.2 Hz, 0.5F),

- 145.6 (t, J = 21.3. Hz, 0.5F); for $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CN}$: -53.1 (m, 2F), -54.5 (m, 2F), -78.2 (m, 2F), -80.1 (m, 3F), -84.1 (m, 2F), -108.4 (m, 2F), -121.2 (m, 1F), -144.6 (m, 1F). HRMS: Calcd for $\text{C}_9\text{F}_{15}\text{I}_2\text{NO}_2$ -I, 565.8734. Found: 565.8716 (M^+ -I). Anal: calcd for $\text{C}_9\text{F}_{15}\text{I}_2\text{NO}_2$: C, 15.60; N, 2.02; I, 36.63. Found: C, 16.26; N, 2.02; I, 35.74.

EXAMPLE 14Reaction of CF_2I_2 with $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$

- A 240 mL of shaker tube was charged with 30.5 g of CF_2I_2 and 50.0 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and cooled to -78°C . After being evacuated at -78°C , the tube was heated at 185°C for 4 hour. 71.3 g of crude products were obtained. Distillation gave 10.3 g of CF_2I_2 , 42 g of adduct, $95-97^\circ\text{C}/5.4$ mmHg. The adduct was a mixture of $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ in a ratio of 5.2 to 1. ^{19}F NMR for $\text{ICF}_2\text{CF}_2\text{CFIOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$: +45.3 (m, 1F), -55.6 (d, J = 204.7 Hz, 1F), -58.9 (ddd, J = 204.7 Hz, J = 27.2 Hz, J = 6.3 Hz, 1F), -69.3 (m, 1F), -79.3 to -80.2 (m, 4F), -89.8 (dm, J = 144.3 Hz, 1F), -101.9 (dm, J = 277.9 Hz, 1F), -104.6 (dt, J = 277.8 Hz, J = 7.7 Hz, 1F), -112.2 (m, 2F), -145.4 (m, 1F); for $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$: -53.2 (m, 2F), -54.5 (m, 2F), -78.2 (m, 2F), -80.1 (m, 5F), -112.4 (m, 2F), -121.2 (m, 1F), -144.6 (m, 1F).

EXAMPLE 15Reaction of CF_2I_2 with $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ at high temperature

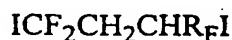
- A 240 mL of shaker tube was charged with 30.6 g of CF_2I_2 and 50.0 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and cooled to -78°C . After being evacuated at -78°C , the tube was heated at 185°C for 4 hour and 240°C for 8 hours. 71.5 g of crude products were obtained. GC indicated a mixture of $\text{ICF}_2\text{CF}_2\text{COF}$, $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, and $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ in a ratio of 4.1:6.6:1 (area ratio). Distillation gave 12.6 of 93% pure $\text{ICF}_2\text{CF}_2\text{COF}$, bp $58-63^\circ\text{C}$, 6.0 g of a mixture of $\text{ICF}_2\text{CF}_2\text{COF}$ and $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, bp $26-100^\circ\text{C}/200$ mmHg, 17.9 g of $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, bp $100-102^\circ\text{C}/200$ mm Hg, 16.7 g of a mixture of 75% $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 16% $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 4.3 g of $(\text{ICF}_2)_2\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$. ^{19}F NMR for $\text{ICF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$: + 45.5 (m, 1F), -58.7 (dm, J = 213.7 Hz, 2F), -60.0 (dm, J = 214 Hz, 2F), -76.9 (m, 3F), -77.9 (dd, J = 139.2 Hz, J = 22.7 Hz, 1F), -79.7 (dm, J = 139.2 Hz, 1F), -122.2 (s, 2F), -133.6 (m, 1F).

What is claimed is:

1. A process for making diiodofluorinated compounds of the formula $\text{ICF}_2(\text{A})_n\text{I}$ wherein n is an integer of at least 1 and each A is CXYCQZ wherein each X , Y , Q , and Z are each independently selected from the group consisting of H , F , Cl , R_F and OR_F , and R_F is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to 20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride, comprising:

reacting an olefin of the formula $\text{CXY}=\text{CQZ}$ with CF_2I_2 at a temperature in the range of from about 120°C to 240°C .

2. The process of Claim 1 wherein the temperature is between about 170°C and about 190°C .
3. The process of Claim 1 wherein n is 1 to 5.
4. The process of Claim 1 wherein n is 1 to 3.
5. The process of Claim 1 wherein n is 1.
6. The process of Claim 1 where X and Y are each F .
7. The process of Claim 6 wherein the olefin is selected from the group consisting of $\text{CF}_2=\text{CFH}$, $\text{CF}_2=\text{CFCF}_3$ and $\text{CF}_2=\text{CH}_2$.
8. The process of Claim 1 wherein the olefin is $\text{CF}_2=\text{CF}_2$ or $\text{CF}_2=\text{CFCl}$.
9. The process of Claim 1 wherein the olefin is a perfluorovinylether of the formula $\text{CF}_2=\text{CFOR}_\text{F}$.
10. A diiodofluorinated compound of formula:



- wherein R_F is a perfluoroalkyl group containing 1 to 20 carbon atoms or a perfluorinated polyether group containing from 2 to 20 carbon atoms wherein one or more of the fluorines of said perfluoroalkyl or perfluorinated polyether group is optionally replaced by a substituent selected from the group consisting of chlorine, bromine, iodine, hydrogen, sulfonyl fluoride, nitrile, ester, acyl chloride and acyl fluoride.

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/US 97/08166

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/278 C07C17/275 C07C19/16 C07C41/30 C07C43/12
C07B37/02

According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2 551 639 A (C.F. FEASLEY ET AL.) 8 May 1951 see claims	1
A	J. ORG. CHEM. (JOCEAH,00223263);84; VOL.49 (1); PP.205-7, UNIV. FLORIDA;DEP. CHEM.; GAINESVILLE; 32611; FL; USA (US), XP002039805 ELSHEIMER S ET AL: "Difluorodiodomethane: its preparation, properties and free-radical reactions" cited in the application see the whole document	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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